

HYDROTREATING IN SUPERCRITICAL MEDIA

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INTRODUCTION

In recent years, supercritical fluid extraction has been a very popular technique for separations. The food and drug industries have used this technique for years on a commercial scale. Recently the energy industries have extended this application to coal liquefaction and oil shale extraction.⁽¹⁻⁵⁾ We, at Phillips, have also found that supercritical extraction of oil shale has improved the oil yield but produced a lower quality liquid product than those from insitu or above ground retorts. We were interested in developing an upgrading technology to upgrade the supercritically extracted (SCE) shale oil to synfuel or clean motor fuels. One of our upgrading projects was to investigate hydrotreating in the presence of the supercritical fluid which is used in the extraction step. If the hydrotreating step can be integrated with the supercritical extraction step, perhaps one can take advantage of, among other things, the pressure and heat available in the extraction step.

Our investigation consisted of essentially two parts. The first part involved the feasibility study of catalytic hydrotreating in the presence of supercritical fluid (in short, supercritical hydrotreating). If hydrotreating in the presence of supercritical media is possible, then we would like to extend the feasibility studies to other heavy feeds, such as topped crude and coal liquids. The second part of our investigation involved the parametric studies to see how reaction parameters effect supercritical hydrotreating.

CONCLUSIONS

From our extensive investigation of the potential of hydrotreating of shale oil under supercritical conditions of the solvent used and then the reaction parameter effects, we would like to make the following conclusions:

A high nitrogen, heavy oil such as shale oil can be hydrotreated under supercritical conditions to yield very low nitrogen fuels and syncrude in one step, depending on the conditions used;

The presence of a light solvent gives a better product and reduces coke formation on the catalyst surface;

- . A non-aromatic solvent such as heptane improves nitrogen removal and reduces hydrogen consumption (from 2600 scf/bbl of shale oil to 1200 scf/bbl);
- . With Arabian topped crude, the solvent loses its enhancement effect for nitrogen removal if the solvent is less than 50 weight percent of the feed;
- . From parameter studies, for an extensive nitrogen removal, a relatively long residence time (30 minutes or longer) is required at 850°F and 1400 psig;
- . And the sulfur was almost completely removed even with the mildest reaction conditions studied.

EXPERIMENTAL

A. Hydrotreating System

A bench scale hydrotreating unit was used for these experiments as shown in Figure 1. The reactor is a 316 stainless steel tube with an inner diameter of one inch and a length of 27.5 inches. The total volume is about 290 ml. The reactor was equipped with a thermocouple well (a 1/4" x 25" stainless steel tube) for temperature measurements. The reactor was first filled with about 90 ml of inert packing, 100 ml of catalyst and the rest with an inert packing again to serve as the preheating zone for the oil and hydrogen. The temperatures were measured by thermocouples placed in the middle of each of the inert beds and the catalyst bed.

B. Feeds

During the course of the investigation the following feeds were used: supercritical extracted coal liquid, supercritical extracted shale oil, Paraho shale oil, and Arabian topped crude (650°F+). Their properties are given in Table 1. To make the feed mixture, the heavy oil was usually dissolved in a solvent such as toluene or n-heptane.

C. Catalysts

The Ni-Mo catalyst was commercially available from Nalco.

D. Catalyst Presulfurization

The catalyst was generally heated to 300°F with nitrogen purging, and then the nitrogen atmosphere was replaced with a flow of 10% H₂S in hydrogen. At the same time, the temperature was slowly increased to 600°F and was kept at this temperature until the catalyst was completely sulfided. The reaction usually takes four hours at 600°F and 100 liter of 10% H₂S in H₂.

RESULTS AND DISCUSSION

In this report the results from the investigation of hydrotreatment of shale oil, Arabian topped crude, and lignite extract (under supercritical conditions) are being discussed. These experiments were carried out to investigate the potential of hydrotreatment in the presence of a light solvent under supercritical conditions for shale oil upgrading and the effect of reaction parameters in supercritical hydrotreating. In other words, these experiments are mainly exploratory in nature to find whether hydrotreatment under supercritical conditions has any advantage in the upgrading of high nitrogen heavy crudes, and if so, how do the major parameters affect the hydrotreatment under these conditions. The first few experiments were carried out with shale oil obtained from supercritical extraction. This shale oil is a very waxy grease and almost fits the definition of a solid. It has a very high nitrogen content (2.3%) and a sulfur content of 0.9%. The hydrogen content in the shale oil is relatively high with H/C atomic ratio of 1.48, equal to that of some petroleum crudes. Only a limited amount of this material was available, so only a few experiments were performed with this shale oil.

A. Supercritical Hydrotreatment of SCE Shale Oil

SCE shale oil was hydrotreated at high severity because of its high nitrogen content and extremely high viscosity (Table 1). The experimental results are shown in Table 2. Based on the shale oil fed, the product distribution is the following: 12% gases, 52% boiling less than 300°F (calculated by difference) and 36% in the heavy oil fraction (>300°F). The elemental analyses of the heavy oil fraction have indicated that better than 99% of the nitrogen was removed. The sulfur removal was equally high. The actual heteroatom removal may even be higher because part of the nitrogen and sulfur found in the heavy oil could be contributed by the presence of dissolved ammonia and hydrogen sulfide gases. No attempt was made to wash out the ammonium sulfide before the elemental analyses were carried out.

For runs 2, 3, 4, and 5 the feed entered the hydrotreater directly from the supercritical extraction unit. The extract contained about 4% shale oil in toluene. Runs 2 and 3 were carried out at 842°F, and Runs 4 and 5, at 750°F. At the lower reaction temperature (750°F), the yield of gases dropped to less than 2%, and the yield of heavy oil fraction increased by about 10%. The extent of nitrogen removal was reduced significantly at the lower temperature. However, the sulfur removal seemed to be unaffected by the lowering of reaction temperature from 842 to 750°F. Thus these experimental results suggest that the supercritically extracted shale oil can be processed to yield very low nitrogen and sulfur fuels or syncrudes.

B. Supercritical Hydrotreatment of Arabian Topped Crude

A series of experiments were performed with Arabian topped crude (650°F+) to investigate the hydrotreatment of high sulfur crudes in the presence of a light solvent under supercritical conditions. The experimental results obtained are summarized in Table 3. The overall results are comparable to those obtained from the supercritical hydrotreatment of SCE shale oil (Run 1). The sulfur removal is

very extensive (about 99% removal, reduced from 3.3% to 0.02%). The nitrogen content in the heavy oil fractions are relatively low, less than 60 ppm for runs with total liquid hourly space velocity (LHSV) of 0.5 (Runs 6 and 7) and about 770 ppm for Run 8 with an LHSV of 1.6. Thus, for extensive nitrogen removal, lower LHSV is needed.

Runs 9 and 10 were carried out to study the effect of an aliphatic solvent such as n-heptane in supercritical hydrotreating of topped crude. Comparing the results from Runs 6 and 7 in which toluene was used as the solvent, the nitrogen contents in heavy oil fractions are much lower for the heptane runs than the toluene ones. The sulfur contents are about the same. Thus, one can conclude that an aliphatic solvent is better solvent for hydrodenitrogenation than the aromatic solvent. The reason is that the aromatic solvent was competing for hydrogenation.

C. Supercritical Hydrotreatment of Lignite Extract

Lignite extract was hydrotreated in the presence of toluene under supercritical conditions (850°F, 1400 psig, 20 wt % lignite in toluene, a hydrogen GHSV of 300, and a LHSV of 1 or 1.6). The results are tabulated in Table 4. The elemental analyses of the heavy oil fraction have indicated the following changes (Runs 13 and 14): nitrogen, reduced from 0.91 to 0.14% and sulfur reduced from 4700 ppm to about 100 ppm.

Run 15 was carried out with a higher LHSV of 1.6, and the results are not too much different from Runs 13 and 14. The heteroatom removals are about the same. The heavy oil fraction, however, was increased to 43% from 30 and 36% (Runs 13 and 14). Thus the conclusion is that the lignite extract, a solid, can also be upgraded to yield a syncrude by the supercritical hydrotreatment process.

D. Supercritical Versus Conventional

A series of hydrotreating experiments were carried out under conventional conditions (without the use of a light solvent). The results are given in Table 5, along with some results obtained from a supercritical hydrotreatment experiment. The experiments performed were not under identical conditions, but they are close enough that the results obtained are valid enough for comparison.

The results from the supercritical hydrotreatment experiments are superior in almost every respect to conventional hydrotreatment experiments (without the use of solvent). Under similar conditions supercritical hydrotreating produced better products, for example: less gas yield (10% vs 25%), more of light oil fraction, <300°F, (55 vs 35%) and less coke formed on the catalyst surface (0.3 vs 3.8% based on the feed). For conventional hydrotreating we had encountered reactor plugging problems when the unit was running more than 196 hours. This problem was not found with supercritical hydrotreating.

E. Reaction Parameter Studies

Experiments were carried out with conventional shale oil (direct retorted Paraho shale oil) for the purpose of studying the

effects of reaction parameters in hydrotreating under supercritical conditions. In one group of experiments, the space velocity was varied (1.6, 3.2, and 5) while the other reaction parameters were kept constant. For temperature studies, the following reaction temperatures were investigated: 700, 750, 800, and 850°F. The pressure effect was examined at four levels -- 1000, 1400, 2000, and 2400 psig at 800°F. We have also studied the effect of solvent to feed ratio and solvent types (saturate vs aromatics).

The liquid hourly space velocities (LHSV, including the solvent) of 1.6, 3.2, and 5 were investigated at 850°F, 1400 psig, 20 wt % Paraho shale oil in toluene. The results are illustrated in Figure 2. With the LHSV of 1.6, the heavy oil fraction is only 34%, but when LHSV is increased to 3.2, the heavy oil fraction increased to 63% and did not change with further increase in LHSV. This seems to suggest that one third of the shale oil can undergo a molecular weight reduction more rapidly (a residence time of about 12 minutes) than the second third, which needs a residence time of up to an hour, while the last third survives longer than one hour.

For heteroatom removal, the results reveal that for a LHSV of 1.6 the nitrogen content in the heavy oil fraction, which is about 34 wt % of the total products, is 360 ppm (1.9% in the feed). Thus, the overall nitrogen removal is greater than 98%. For LHSV of 3.2 the nitrogen content in the heavy oil is increased to about 6,000 ppm. With a further increase in LHSV to 5, there seems to be very little change in the nitrogen removal. The sulfur removal is very rapid. Even with the LHSV of 5, there is only 53 ppm sulfur in the heavy oil.

Figure 3 illustrates the results from reaction temperature studies. The reaction temperatures used ranged from 700 to 850°F, with an increment of 50°F. The sulfur seems to be removed rather easily even at 700°F (from 7000 ppm in the feed to 200 ppm in the heavy oil fraction) or 97% removal. At higher temperatures the sulfur content in the heavy oil is much lower (~100 ppm). On the other hand, the nitrogen removal requires a much higher temperature. This, of course, is not surprising. For the purpose of obtaining relatively clean syncrude, we probably have to operate at high temperature (800°F) and low space velocity (<1.6).

The yield of heavy oil increases with a decrease of reaction temperature (Figure 3). For example, with the reaction temperature of 850°F, the heavy oil is only about 30% of the total products. While at the other extreme, that is, with the reaction temperature of only 700°F, the heavy oil fraction represents 90% of the whole products. Thus the higher temperature is necessary for the production of light products.

The effect of pressure on HDN and heavy oil yield in supercritical hydrotreating of shale oil is given in Figure 4. The experimental conditions used for these experiments are: 800°F, hydrogen GHSV of 600, LHSV of 1.6, 20 wt % shale oil in toluene, and reaction pressure of 1000-2400 psig. The nitrogen content in the heavy oil fractions have revealed that nitrogen removal increases with increasing reaction pressure. At the highest pressure studied (2400 psig), the nitrogen content in the heavy oil is only about 300 ppm. This is

about 98% nitrogen removal. The nitrogen removal decreased with the decrease in reaction pressure.

The effect of crude oil concentration in the feed was investigated with Arabian 650°F+ topped crude. Three concentrations (20, 50, and 80% of topped crude in toluene) were chosen, while the other experimental conditions were kept constant (see Figure 5 and Table 3). Both the nitrogen removal and heavy oil conversion are more extensive when the crude is hydrotreated at a more diluted level such as 20%. The heteroatom removal is reduced at higher crude concentrations and levels off at 50% or higher. The yield of the heavy oil fraction increases with increasing concentration of crude in the toluene.

The use of a non-aromatic solvent as the supercritical hydrotreating solvent was studied first with Arabian topped crude and then with Paraho shale oil in hope of reducing hydrogen consumption. The results are tabulated in Table 6. Run 16 used toluene as the solvent, and Runs 17 and 18 used n-heptane. The experimental results have shown that nitrogen removal is slightly higher with n-heptane than with toluene (a more significant difference was found with Arabian topped crude as the feed). The yield of heavy oil fraction is lower (37% for heptane and 47% for toluene) for the saturated solvent. This means hydrocracking was more extensive. The H/C atomic ratio of the heavy oil is also much higher for heptane than for toluene. Thus hydrogenation is deeper with heptane as the solvent. Hydrogen consumption is also significantly reduced, 1200 scf/bbl of shale oil for heptane versus 2600 scf/bbl for toluene. With everything considered, heptane is by far a better hydrotreating solvent than toluene.

To sum up, extensive research has been done to study the potential of supercritical hydrotreatment for the upgrading of shale oil and then the effects of major reaction parameters in supercritical hydrotreating. The experimental results have demonstrated that hydrotreatment in the presence of a light solvent and under supercritical conditions has some advantages over conventional hydrotreatment. Compared with conventional process, the supercritical hydrotreating process yields a better product (less gas, more distillates) and produces less coke on the catalyst. Supercritical hydrotreating appears to be a very versatile process which can be optimized for a variety of different products. This process can be applied equally well for upgrading other heavy oils, such as coal liquids and high sulfur petroleum topped crudes, to yield low nitrogen and sulfur syncrudes and transportation fuels.

Saturated solvent such as n-heptane has been examined as the process solvent. Saturated solvent seems to do better in terms of nitrogen removal and hydrogen consumption. With either solvent, sulfur removal was very extensive. From reaction parameter studies, a relatively high severity is required for extensive nitrogen removal.

TABLE I
FEED PROPERTIES

Feed	Elemental Analyses				H/C
	C	H	N	S	
SCE Shale Oil ¹	84.5	10.4	2.3	1.0	1.48
Paraho Shale Oil ²	84.5	11.7	1.9	0.7	1.66
Arabian Topped Crude ³	84.9	11.3	0.18	3.3	1.60
Lignite Extract ⁴	82.0	9.3	0.91	0.47	1.36

1. The SCE shale oil is a waxy black semi-solid.
2. Paraho shale oil has about 70 Vol % of 650⁺ F material.
3. Totally 650⁺ F material.
4. Hard solid at room temperature.

TABLE II
SUPERCritical HYDROTREATMENT OF SCE SHALE OIL*

Run No. ^a	Temp. °F	LHSV	Gases	Heavy Oil (>300 F)		
			(C ₁ -C ₄)Wt%	Wt. %	N(ppm)	S(%)
1	842	0.5	12	36	52	0.03
2	842	1.6	--	46	150	0.03
3	842	1.6	--	44	150	0.02
4	750	1.6	<2	54	2300	0.08
5	750	1.6	<2	32 ^b	2000	0.04

*A total operating pressure of 1400 psig and sulfided Ni-Mo/Al₂O₃ catalyst were used in these experiments. The shale oil has the following elemental analyses: C, 84.5; H, 10.4; N, 2.3; S, 1.0.

^aThe feed for Run 1 consisted of 20 wt % shale oil in 80 wt % toluene, but for Runs 2 to 5, the feed was only 4% shale oil in toluene.

^bIn this run this fraction was distilled up to 400°F instead of 300°F as usual.

TABLE III

SUPERCRITICAL HYDROTREATMENT OF ARABIAN TOPPED CRUDE (ATC)
(850°F, 1400 psig, H₂ GHSV 300, Nalco Ni-Mo Catalyst)

<u>Run No.</u>	<u>Feed^A</u> Wt % ATC in Solvent	<u>LHSV</u>	<u>Heavy Oil</u>		
			<u>Wt %</u>	<u>N (%)</u>	<u>S (%)</u>
6	20	0.5	34	0.006	0.02
7	20	0.5	34	0.004	0.02
8	20	1.6	59	0.068	0.04
9	20	0.5	33	2 ppm	0.02
10	20	0.5	36	3 ppm	0.03
11	50	1.6	64	0.094	0.17
12	80	1.6	72	0.094	0.13

^ASolvent for Runs 9 and 10 was n-heptane; for others toluene was used.

TABLE IV

SUPERCRITICAL HYDROTREATMENT OF LIGNITE EXTRACT

<u>Run No.</u>	<u>LHSV</u>	<u>Heavy Oil Fraction (>300°F)</u>		
		<u>Wt %</u>	<u>N(ppm)</u>	<u>S(ppm)</u>
13	1	30	1530	150
14	1	36	1400	90
15	1.6	43	1180	100

Lignite Extract Feed	100	9100	4700
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Conditions: 850°F, 1400 psig, 300 H₂ GHSV, 20 wt %
lignite extract in toluene, Nalco Ni-Mo catalyst.

TABLE V

**COMPARISON OF CONVENTIONAL AND
SUPERCRITICAL HYDROTREATING**

(Conditions: 1400 psig, 850°F,
H₂ GSHV=300, Nalco Ni-Mo)

<u>FEED</u>	<u>NO SOLVENT</u>	<u>WITH SOLVENT</u>
	<u>SHALE OIL (NEAT)</u>	<u>20% SHALE OIL IN TOLUENE</u>
LHSV	0.3	TOTAL = 1.6 SHALE OIL = 0.32
GAS YIELD (Wt %)	25	10
LIGHT (Wt %)	35	55
HEAVY OIL (Wt %)	35	35
COKE (Wt %)	3.8	0.3

TABLE VI

**SUPERCRITICAL HYDROTREATMENT OF SHALE OIL IN
TOLUENE OR n-HEPTANE**

(850°F, 1400 psig, Nalco Ni-Mo catalyst,
1.6 LHSV, 300 H₂ GSHV)

<u>Run No.</u>	<u>Feed</u>	<u>Heavy Oil (>300°F)</u>				<u>H₂ Consumption</u> <u>Scf/Bbl</u>
		<u>Wt %</u>	<u>N(ppm)</u>	<u>S(%)</u>	<u>H/C</u>	
16	20% Shale Oil in Toluene	57	3149	<0.01	1.66	2600 ± 200
17	20% Shale Oil in Heptane	36	1595	<0.01	1.79	1200 ± 100
18	20% Shale Oil in Heptane	37	1890	<0.01	1.82	1200 ± 100

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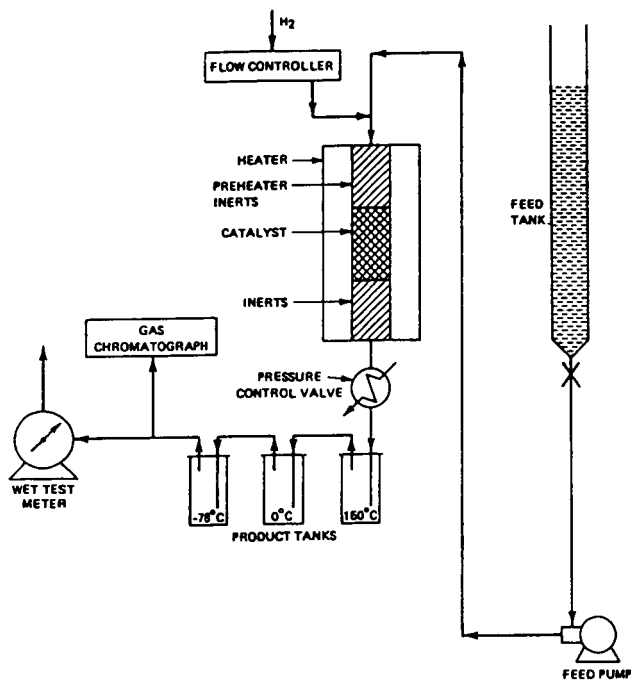


FIGURE 1
SUPERCRITICAL HYDROTREATING SYSTEM

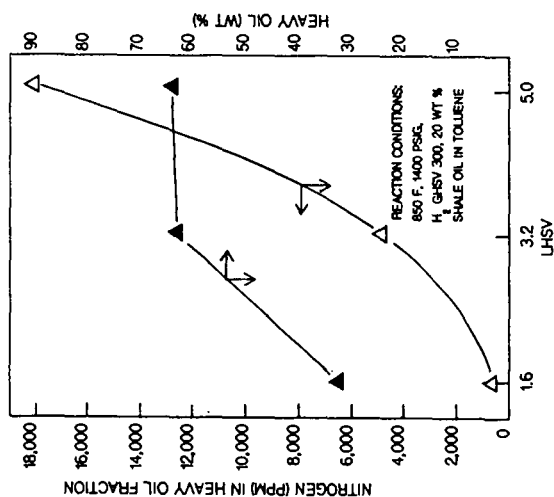


FIGURE 2
SPACE VELOCITY EFFECTS ON
SUPERCRITICAL HYDROTREATMENT OF SHALE OIL

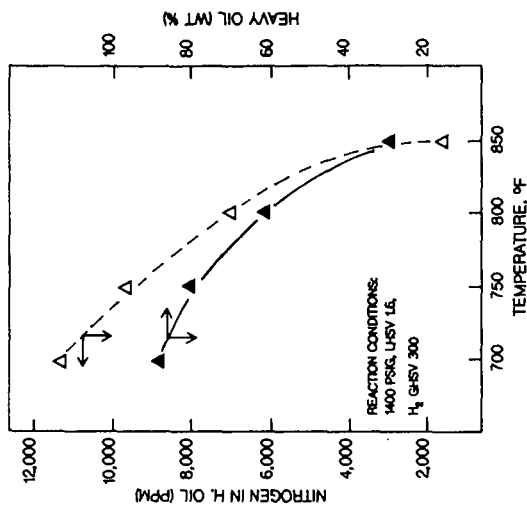


FIGURE 3
EFFECT OF TEMPERATURE ON
SUPERCRITICAL HYDROTREATMENT OF SHALE OIL

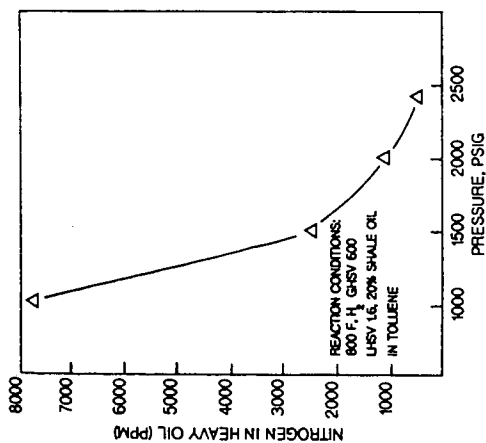


FIGURE 4

EFFECT OF PRESSURE ON
SUPERCritical HYDROTREATMENT OF SHALE OIL

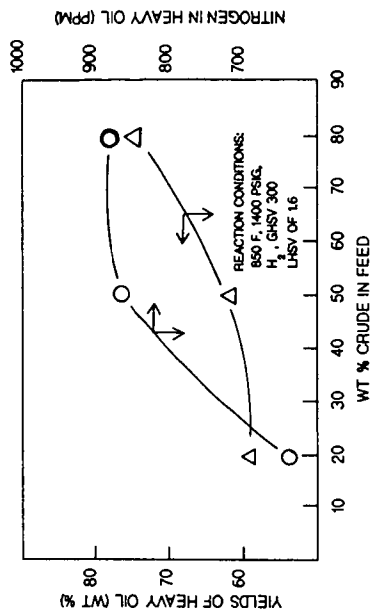


FIGURE 5

EFFECT OF OIL CONCENTRATION
IN SUPERCritical HYDROTREATMENT OF
ARABIAN TOPPED CRUDE